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Fe_3BO_5@carbon core–shell urchin-like structures prepared via a one-step co-pyrolysis method

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ABSTRACT

Urchin-like Fe_3BO_5@carbon core–shell structures (defined as "FBOC") have been fabricated by a one-step co-pyrolysis method using boric acid and ferrocene as raw materials. This complex architecture is composed of high-density Fe_3BO_5@carbon nanocables that stand on Fe_3BO_5@carbon structure. After removing the Fe_3BO_5, hollow urchin-like carbon material was obtained. In the reaction process, B_2O_3 and H_2O that decomposed from H_3BO_3 have synergistic effect on the formation of urchin-like structures. It is found that urchin-like structures can also be obtained when other materials that can release H_2O and B_2O_3 react with ferrocene. The influences of the reaction conditions on the preparation of FBOC have been discussed in detail.

1. Introduction

Ferroferriborate (Fe_3BO_5), as a mixed valence compound, displays many interesting properties, such as catalytic oxidation of small organic molecules (ethyl acetate and methanol) [1,2], paramagnetic–antiferromagnetic transition at 114 K and a charge ordering crossover at 220 K [3,4]. It could also be applied as stuff in studies of the mechanisms of electron interactions in transition metal oxides.

Nanoscale Fe_3BO_5 are apt to be agglomerate, and their structures are easily collapsed even in a mild reducing atmosphere at 500 °C, which would hinder their wide applications. Surface modification is considered to be an effective way to prevent the agglomeration. Fe_3BO_5 nanorods coated with silica composite have been produced, their morphology and performance were well remained even after high temperature treatment [5]. Besides silica, amorphous carbon has also been widely used as a protective material to improve the corrosion resistance, thermal stability, adsorbability, or electronic properties of the materials such as polymers, ceramics, metals, and oxides [6].

As is known that ferrocene could easily decompose into Fe nuclei and carbon species at relatively low temperature (≥500 °C), therefore, ferrocene has been widely used for the synthesis of carbon materials such as CNTs, hollow carbon spheres, carbon encapsulates, and iron-related carbon composite materials [7–10]. In this experiment, ferrocene and boric acid were used as raw materials for the synthesis of FBOC. The average size of the prepared FBOC is 3 μm. In addition, hollow urchin-like carbon materials were obtained after the inside Fe_3BO_5 were removed by HCl at 80 °C for 5 h. This kind of FBOC may offer an opportunity to investigate the magnetic and catalytic properties of the composites, and the hollow carbon materials may be used as templates to synthesize other kinds of urchin-like materials or composites.

2. Experimental section

All the chemical regents used here were analytical grade. In a typical procedure, ferrocene (0.005 mol, 0.932 g) and boric acid (0.01 mol, 0.632 g) were put into a stainless steel autoclave of 20 ml capacity. The autoclave was sealed and loaded into an electronic furnace at 150 °C, and then the temperature of the furnace was increased to 600 °C at the rate of 10 °C/min and maintained at 600 °C for 10 h before being air-cooled to room temperature. It was found that the final product in the autoclave was black powder. The black powder was collected and divided into two parts: one part was washed with distilled water and absolute ethanol several times to obtain the urchin-like Fe_3BO_5@carbon core–shell nanostructure material; the other part was heated in dilute HCl solution at 80 °C for 5 h to obtain hollow urchin-like carbon material. After that, the two samples were dried in a vacuum box at 60 °C for 10 h and collected for characterization. Microstructure and phase structure were characterized with SEM, HRTEM, XRD and TEM techniques.

3. Results and discussion

Fig. 1a and b shows the X-ray powder diffraction (XRD) patterns of the FBOC before and after acid treatment, respectively. According to Fig. 1a, all the distinguished diffraction peaks can be indexed as Fe_3BO_5 (JCPDS Card No. 25-0395). Fig. 1b shows the XRD pattern of

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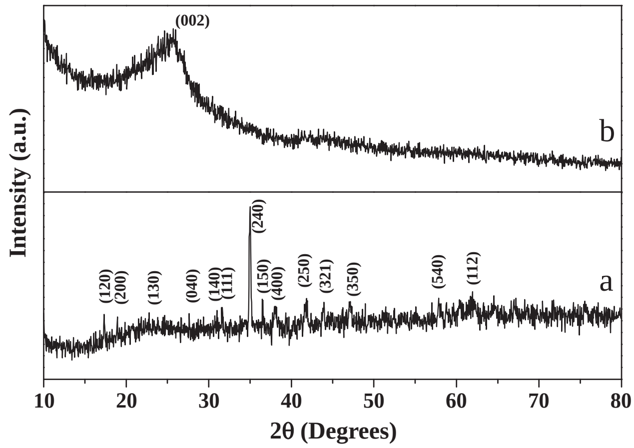

Fig. 1. (a) The XRD patterns of FBOC before/(b) after the acid treatment.

the product after heated in diluted HCl solutions, which can be attributed to carbon materials. Fig. 2 shows the Raman spectrum of FBOC after HCl acid treatment. There are two obvious peaks at 1340 and 1600 cm^{-1}. The peak at 1600 cm^{-1} (G-band) can be indexed as the stretching modes of C=C bonds of graphite, while the peak centered at 1340 cm^{-1} (D-band) corresponds to the vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite [11]. These results completely prove that the as-obtained products are carbon materials.

The thermal stability of the as-obtained sample was studied by TGA (ESI-Fig. 1). The result indicates that below 440 °C the product is stable in ambient atmosphere, which can be attributed to the protection of outside carbon shells. From the TGA curve, one can observe that a rapid weight loss emerged in the temperature range of 440–620 °C, and this result is closed to that of the previous reports of carbon [12].

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) observations indicate that the products are composed of a large quantity of urchin-like structures with average size of 3 μm. Fig. 3 shows typical TEM and SEM images of the as-obtained FBOC. These FBOC are composed of spheres and cables: spheres act as the cores and Fe_3BO_5@carbon cables as the surrounding spines (Fig. 3a). Most of those "spines" are Fe_3BO_5@carbon nanocables. Fig. 3b shows a close observation of nanocables. The distinct contrast suggests their core–shell nanostructure. The surfaces of the shells are smooth and 11 nm thick. The lengths of the nanocables are ranging from 50 to 950 nm. The HRTEM analysis offers more detailed information of the Fe_3BO_5 nanowires (Fig. 3c). The lattice fringe observed in this image is 0.51 nm, which corresponds to the interplanar spacing of the (200) plane of Fe_3BO_5. This is consistent with the previous report of the plywood-like Fe_3BO_5 nanorods [13]. After acid treatment, hollow carbon materials were obtained as shown in Fig. 3d. The morphology and size of the hollow carbon materials were the same as the FBOC.

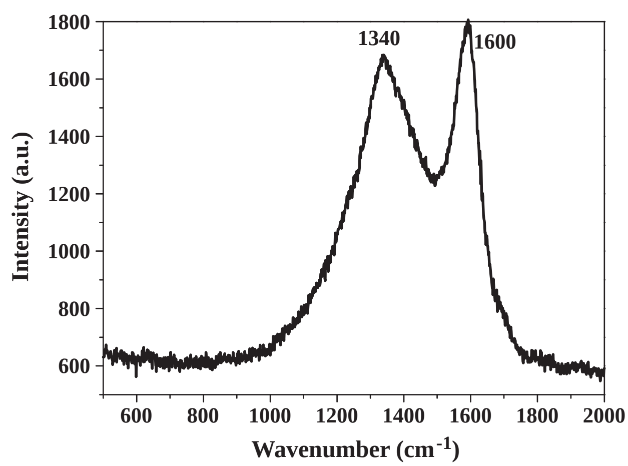

Fig. 2. The Raman spectrum of the hollow urchin-like carbon material.

The panoramic morphology of FBOC architectures shown in Fig. 3e reveals that the samples have urchin-like shapes with an average size of 3 μm, which agrees with the TEM observations. The magnified view of an individual FBOC clearly reveals the exact configuration about the FBOC (Fig. 3f). It is found that some of the "spines" were broken, which may be caused by ultrasonic process during the preparation of the SEM sample.

A series of contrast experiments were carried out through similar processes to investigate the effects of reaction parameters (i.e., reaction temperature, reaction time, and boron source.) on the formation of FBOC. Keeping other conditions unchanged, when boric acid was replaced by equimolar amount of other borates, such as ammonium tetraborate hydrate, magnesium metaborate, sodium tetraborate decahydrate and lithium tetraborate, we discovered that only ammonium tetraborate hydrate could produce urchin-like structure materials. The reason may be that ammonium tetraborate hydrate as well as boric acid can easily decompose and release B_2O_3 and H_2O. The released B_2O_3 and H_2O might play crucial roles during the formation of urchin-like Fe_3BO_5. It is also proved by the fact that when the same amounts of B_2O_3, H_2O and ferrocene were used as the initial material, urchin-like structure materials were also obtained. But if only B_2O_3 or H_2O reacted with ferrocene, urchin-like structure could not be gained. Therefore, we can reasonably conclude that B_2O_3 and H_2O have synergistic effect on the formation of FBOC. The reaction temperature is another determining factor on the formation of FBOC. If the reaction temperature was set at 500 °C, a mixture of the ball-like structures with nanorod bundles, and branched cables was observed (ESI-Fig. 2a). When the reaction temperature was set at 700 °C, the proportion of urchin-like structures was reduced while branch-like structures were detected (ESI-Fig. 2b). When reducing the reaction time, FBOC co-existed with particles were observed; if prolonging reaction time, no significant difference on the structures was found. Hereby, 600 °C and 10 h are the optimal parameters for the production of FBOC.

According to the above results and analysis, the possible formation mechanism of FBOC was proposed. It is well known that both ferrocene and H_3BO_3 are readily decomposed with increasing temperature and release Fe, H_2O and B_2O_3, respectively. A part of the Fe atoms would react with H_2O to form Fe_3O_4 nuclei, and then the remaining Fe, H_2O and B_2O_3 would interact and form Fe_3BO_5 nanowire on the Fe_3O_4 nuclei. This process is similar with the previous report about the preparation of Fe_3BO_5 nanorods [5]. At the end of this experiment, ferrocene was converted into Fe_3BO_5, C and residual gasses. It is reasonable to speculate that carbon atoms are coated on the surface of the Fe_3BO_5 to diminish the surface energy. However, the exact formation mechanism of the as-obtained FBOC still needs further research.

4. Conclusions

In this study, we have successfully synthesized FBOC with high yield by the pyrolysis of ferrocene and boric acid mixture in a stainless steel autoclave. After HCl treatment, hollow urchin-like carbon materials were obtained. Their size and structure were studied by SEM, TEM and HRTEM. The XRD and Raman spectra confirmed that both FBOC and hollow urchin-like carbon materials exhibit high purity. Furthermore, this kind of FBOC may offer an opportunity to

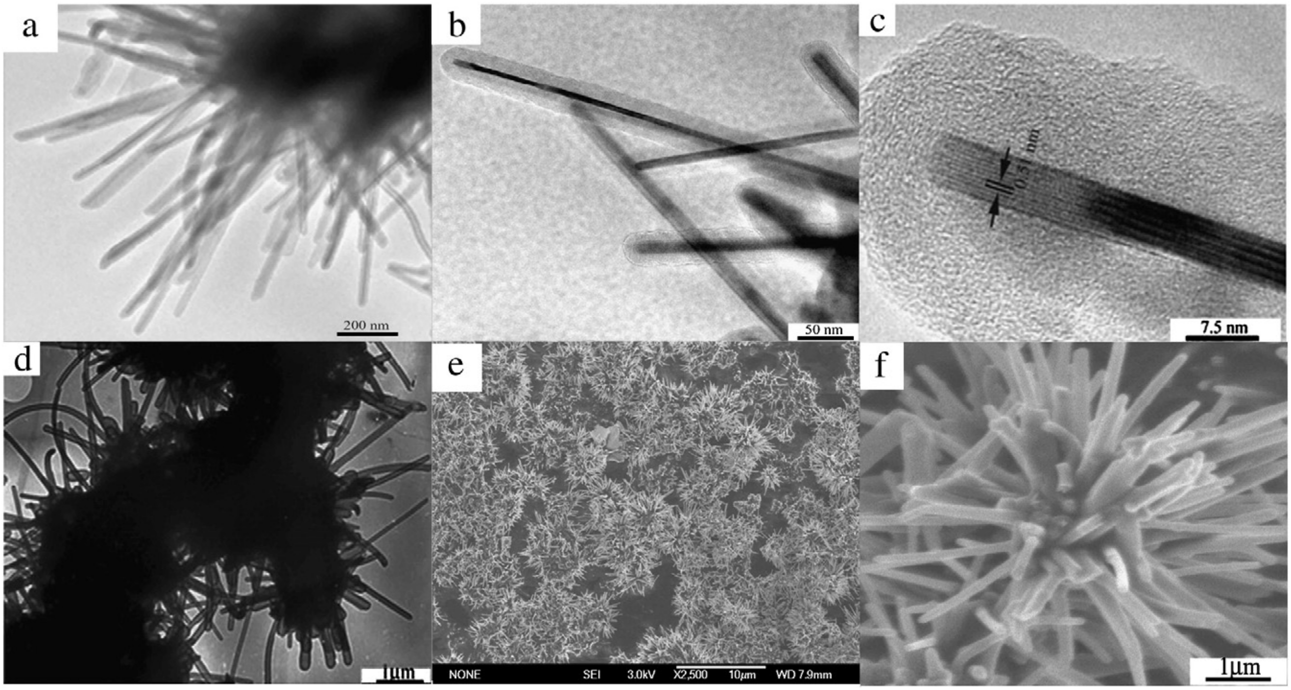

Fig. 3. Low-magnification (a) and high-magnification (b) TEM images of FBOC. (c) HRTEM image of the Fe_3BO_5. (d) Low-magnification of the hollow carbon materials. (e) The SEM images of FBOC and (f) single FBOC prepared at 600 °C.

investigate dimensionally confined systems, and the hollow carbon material may be used as template to synthesize other kinds of urchin-like materials.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.matlet.2011.05.039.

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